



Europäisches
Patentamt

European
Patent Office

Office européen
des brevets

08.04.2004

Bescheinigung

Certificate

Attestation

REC'D 02 JUN 2004

WIPO

PCT

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

03405266.2

**PRIORITY
DOCUMENT**

SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk



Anmeldung Nr:
Application no.: 03405266.2
Demande no:

Anmeldetag:
Date of filing: 16.04.03
Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

Ciba Specialty Chemicals Holding Inc.
Klybeckstrasse 141
4057 Basel
SUISSE

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se référer à la description.)

Radiation curable ink-jet containing an alpha hydroxy ketone as photoinitiator

In Anspruch genommene Priorität(en) / Priority(ies) claimed / Priorité(s)
revendiquée(s)
Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/
Classification internationale des brevets:

C09D11/00

Am Anmeldetag benannte Vertragstaaten/Contracting states designated at date of
filing/Etats contractants désignées lors du dépôt:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LU MC NL
PT RO SE SI SK TR LI

Radiation curable ink-jet ink containing an alpha hydroxy ketone as photoinitiator.

The present invention relates to a radiation curable ink-jet ink containing an alpha hydroxy ketone as photoinitiator.

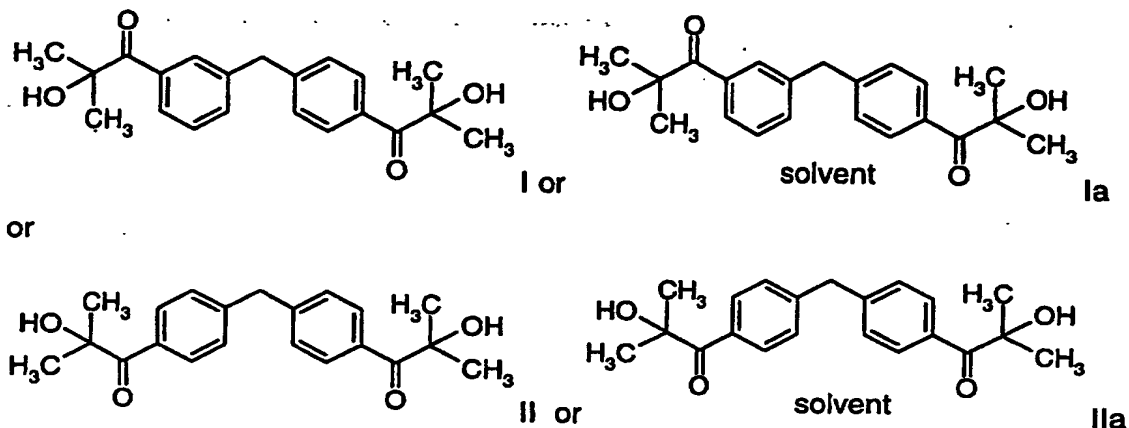
In the ink-jet process, an image is produced by ejecting ink droplets onto a recording material through a nozzle. The inks used in various ink jet printers can be classified as either dye-based or pigment-based.

A radiation curable ink jet ink composition may in general contain one or more radiation curable monomers, prepolymers or oligomers or reactive diluents; one or more photoinitiators, colorants and other additives. In formulating the final ink jet ink compositions of the present invention, certain physical properties should be satisfied. For example, ink compositions for use in ink jet recording processes should have appropriate viscosity of less than 50 mPas at ambient temperature. The properties of the ink such as viscosity, gloss, and crosslink density can be controlled by varying the types and/or proportions of reactive diluents used in the formulation.

Useful photoinitiators are, for example, alpha-hydroxyketones, such as 1-hydroxycyclo-hexyl phenyl ketone (IRGACURE 184), 2-hydroxy-2-methyl-1-phenyl-1-propanone (DAROCUR 1173), 1-[4-(2-hydroxyethoxy)-phenyl]-2-hydroxy-2-methyl-1-propane-1-one (IRGACURE 2959) or poly {2-hydroxy-2-methyl-1-[4-(1-methylvinyl)phenyl]propan-1-one (available commercially as Esacure KIP 150, Fratelli Lamberti). IRGACURE and DAROCUR are commercial products of Ciba Specialty Chemicals Inc.

It has been found that a photoinitiator as disclosed in PCT Application No. EP/02/12160 improves the cure speed in UV curable inks.

Thus, the invention relates to an ultraviolet curable ink jet ink composition comprising a photopolymerizable monomer, oligomer or prepolymer; a colorant and a compound of the formula I or II or Ia or IIa



or mixtures thereof.

For the preparation of solvent-containing crystals there are suitable polar solvents, for example water, aliphatic alcohols, for example methanol, ethanol; amines, for example tertiary amines. The solvent is preferably water. The content of solvent (water) is from 2 to 8 % by weight, preferably from 4 to 6 % by weight.

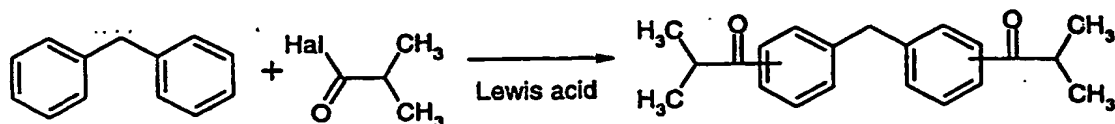
In the preparation process, solvent-containing (water-containing) crystalline isomeric mixtures of the compounds of formulae Ia and IIa are initially formed, from which solvent-free isomeric mixtures are obtained by drying using drying agents.

The isomeric mixtures may contain the meta-para compound and the para-para compound in any ratio by weight. However, preference is given to an isomeric mixture having a content of para-para compound of from 99.9 to 25 % by weight and having a content of meta-para compound of from 0.1 to 75 % by weight. Special preference is given to an isomeric mixture having a content of para-para compound of from 99.9 to 70 % by weight and having a content of meta-para compound of from 0.1 to 30 % by weight.

Especially preferred is a mixture of compound Ia and IIa having a content of compound Ia of 1-2% and water content of 4-6%.

The preparation of the isomeric mixture is carried out according to the following scheme:

a) Friedel-Crafts acylation



- b) chlorination to bis(α -chloroisobutyryl)diphenylmethane,
- c) hydrolysis to bis(α -hydroxyisobutyryl)diphenylmethane,
- d) further processing to the solvent-containing crystalline isomeric mixture,
- e) where appropriate, drying to form the solvent-free crystalline isomeric mixture.

Suitable **monomers** include those compounds which have at least one carbon-carbon unsaturated bond. Non limiting examples of such monomers include:

(meth)acrylic acid and salts thereof;

(meth)acrylic acid esters such as alkylesters e.g. methyl, ethyl, 2-chloroethyl, N-dimethyl-aminoethyl, n-butyl, isobutyl-, pentyl, hexyl, cyclohexyl, 2-ethylhexyl, octyl, isobornyl [2-exo-bornyl] esters;

phenyl, benzyl-, and o-, m- and p-hydroxyphenyl esters;

hydroxyalkylesters e.g. 2-hydroxyethyl, 2-hydroxypropyl, 4-hydroxybutyl, 3,4-dihydroxybutyl or glycerol [1,2,3-propanetriol] esters;

epoxyalkylesters e.g. glycidyl, 2,3-epoxybutyl, 3,4-epoxy butyl, 2,3-epoxycyclohexyl, 10,11-epoxyundecyl esters;

(meth)acrylamides, N-substituted (meth)acrylamides, e.g. N-methylolacrylamide, N-methylol-methacrylamide, N-ethylacrylamide, N-ethylmethacrylamide, N-hexylacrylamide, N-hexyl-methacrylamide, N-cyclohexylacrylamide, N-cyclohexylmethacrylamide-, N-hydroxyethyl-acrylamide, N-phenylacrylamide, N-phenylmethacrylamide, N-benzylacrylamide, N-benzyl-methacrylamide, N-nitrophenylacrylamide, N-nitrophenylmethacrylamide, N-ethyl-N-phenyl-acrylamide, N-ethyl-N-phenylmethacrylamide, N-(4-hydroxyphenyl)acrylamide, and N-(4-hydroxyphenyl)methacrylamide, IBMAA (N-isobutoxymethyl acrylamide),

(meth)acrylnitriles;

unsaturated acid anhydrides such as itaconic anhydride, maleic anhydride, 2,3-dimethyl maleic anhydride, and 2-chloromaleic anhydride,

unsaturated acid esters such as maleic acid esters, phthalic acid esters, itaconic acid esters, [methylene succinic acid esters];

styrenes, such as methyl styrene, chloromethyl styrene, and o-, m-, and p-hydroxystyrene, divinylbenzene;

vinyl chloride and vinylidene chloride;

vinyl ethers such as isobutyl vinyl ether, ethyl vinyl ether, 2-chloroethyl vinyl ether, hydroxyethyl vinyl ether, propyl vinyl ether, butyl vinyl ether, isobutyl vinyl ether, octyl vinyl ether and phenyl vinyl ether;

vinyl and allyl esters such as vinyl acetate, vinyl acrylate, vinyl chloroacetate, vinyl butyrate and vinyl benzoate, divinyl succinate, diallyl phthalate, triallyl phosphate;

isocyanurates such as triallyl isocyanurate and tris(2-acryloyloylethyl) isocyanurate;

N-vinyl heterocyclic compounds, N-vinylpyrrolidone or suitably substituted vinylpyrrolidones, N-vinylcarbazol, N-vinylcaprolactam or suitably substituted vinylcaprolactames, 4-vinylpyridine.

Typical examples for esters are:

diacrylates such as 1,6-hexane diol diacrylate (HDDA), ethylene glycol diacrylate, propylene glycol diacrylate, dipropylene glycol diacrylate, tripropylene glycol diacrylate, neopentyl glycol diacrylate, hexamethylene glycol diacrylate and bisphenol A diacrylate, trimethylolpropane triacrylate, trimethylolethane triacrylate, trimethylolpropane trimethacrylate, trimethylolethane trimethacrylate, tetramethylene glycol dimethacrylate, triethylene glycol dimethacrylate, tetraethylene glycol diacrylate, pentaerythritol diacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, dipentaerythritol diacrylate, dipentaerythritol triacrylate, dipentaerythritol tetraacrylate, dipentaerythritol pentaacrylate, dipentaerythritol hexaacrylate, tripentaerythritol octaacrylate, pentaerythritol dimethacrylate, pentaerythritol trimethacrylate, dipentaerythritol dimethacrylate, dipentaerythritol tetramethacrylate, tripentaerythritol octamethacrylate, pentaerythritol diitaconate, dipentaerythritol trisitaconate, dipentaerythritol pentaitaconate, dipentaerythritol hexaitaconate, ethylene glycol diacrylate, 1,3-butanediol diacrylate, 1,3-butanediol dimethacrylate, 1,4-butanediol diitaconate, sorbitol triacrylate, sorbitol tetraacrylate, pentaerythritol-modified triacrylate, sorbitol tetramethacrylate, sorbitol pentaacrylate, sorbitol hexaacrylate, oligoester acrylates and methacrylates, glycerol di- and triacrylate, 1,4-cyclohexane diacrylate, bisacrylates and bismethacrylates of polyethylene glycol having a molecular weight of from 200 to 1500, and mixtures thereof.

The following esters of alkoxylated polyols are also suitable: glycerol ethoxylate triacrylate, glycerol propoxylate triacrylate, trimethylolpropane ethoxylate triacrylate, trimethylolpropane propoxylate triacrylate, pentaerythritol ethoxylate tetraacrylate, pentaerythritol propoxylate

triacrylate, pentaerythritol propoxylate tetraacrylate, neopentyl glycol ethoxylate diacrylate, neopentyl glycol propoxylate diacrylate.

Non limiting examples of higher molecular weight (oligomeric) polyunsaturated compounds (also known as prepolymers) are:

Esters

Esters of ethylenically unsaturated mono- or poly-functional carboxylic acids and polyols or polyepoxides, and polymers having ethylenically unsaturated groups in the chain or in side groups, e.g. unsaturated polyesters, polyamides and polyurethanes and copolymers thereof, alkyd resins; polybutadiene and butadiene copolymers, polyisoprene and isoprene copolymers, polymers and copolymers having (meth)acrylic groups in side chains such as methacrylated urethanes and also mixtures of one or more such polymers.

Examples of suitable mono- or poly-functional unsaturated carboxylic acids are acrylic acid, methacrylic acid, crotonic acid, itaconic acid, cinnamic acid, maleic acid, fumaric acid, itaconic acid, and unsaturated fatty acids such as linolenic acid and oleic acid. Acrylic and methacrylic acid are preferred.

It is also possible, however, to use saturated di- or poly-carboxylic acids in admixture with unsaturated carboxylic acids. Examples of suitable saturated di- or poly-carboxylic acids include, for example, tetrachlorophthalic acid, tetrabromophthalic acid, phthalic anhydride, adipic acid, tetrahydrophthalic acid, isophthalic acid, terephthalic acid, trimellitic acid, heptanedicarboxylic acid, sebacic acid, dodecanedicarboxylic acid, hexahydrophthalic acid, etc.

Suitable polyols are aromatic and, especially, aliphatic and cycloaliphatic polyols. Examples of aromatic polyols are hydroquinone, 4,4'-dihydroxydiphenyl, 2,2-di(4-hydroxyphenyl)propane, and novolaks and resols. Examples of polyepoxides are those based on the said polyols, especially the aromatic polyols and epichlorohydrin. Also suitable as polyols are polymers and copolymers that contain hydroxyl groups in the polymer chain or in side groups, e.g. polyvinyl alcohol and copolymers thereof or polymethacrylic acid hydroxyalkyl esters or copolymers thereof. Further suitable polyols are oligoesters having hydroxyl terminal groups.

Examples of aliphatic and cycloaliphatic polyols include alkylenediols having preferably from 2 to 12 carbon atoms, such as ethylene glycol, 1,2- or 1,3-propanediol, 1,2-, 1,3- or 1,4-butanediol, pentanediol, hexanediol, octanediol, dodecanediol, diethylene glycol, triethylene glycol, polyethylene glycols having molecular weights of preferably from 200 to 1500, 1,3-cyclopentanediol, 1,2-, 1,3- or 1,4-cyclohexanediol, 1,4-dihydroxymethylcyclohexane, glycerol, tris(β -hydroxyethyl)amine, trimethylolethane, trimethylolpropane, pentaerythritol, dipentaerythritol and sorbitol.

The polyols may be partially or fully esterified by one or by different unsaturated carboxylic acid(s), it being possible for the free hydroxyl groups in partial esters to be modified, for example etherified, or esterified by other carboxylic acids.

Preferred are:

(meth)acrylated epoxy esters

(meth)acrylated polyesters or vinyl-ether-group-containing polyesters,

(meth)acrylated polyurethanes, polyethers and polyols.

Aminoacrylates

A preferred component used in UV-curable inkjet are acrylates which have been modified by reaction with primary or secondary amines, as described, for example, in US 3 844 916 of Gaske, in EP 280 222 of Weiss *et al.*, in US 5 482 649 of Meixner *et al.* or in US 5 734 002 of Reich *et al.* Such amine-modified acrylates are also termed **aminoacrylates**. It is known that in the presence of aminoacrylates UV-curable systems show an increased curing performance. They are useful to overcome the oxygen inhibition typically observed for radical induced polymerization reactions, especially for low viscous systems like UV-curable inkjet. Aminoacrylates are obtainable, for example, under the name EBECRYL 80, EBECRYL 81, EBECRYL 83, EBECRYL P115, EBECRYL 7100 from UCB Chemicals, under the name Laromer PO 83F, Laromer PO 84F, Laromer PO 94F from BASF, under the name PHOTOMER 4775 F, PHOTOMER 4967 F from Cognis or under the name CN501, CN503, CN550 from Cray Valley or under the tradename Genomer 5275 from Rahn AG.

It will be clear that all these cited monomers, prepolymers, polymers and oligomers can be used in admixture.

Especially emphasized are cationic-curable compositions having a low viscosity which comprise at least one aliphatic or aromatic epoxide, at least one polyol or polyvinyl polyols as mentioned above, and at least one cation-generating photoinitiator. A number of these epoxides are well known in the art and are commercially available.

The photoinitiators that can be used in the cationic photocurable compositions are, for example, aryl iodonium salts and aryl sulfonium salts.

US6306555 describes diaryliodonium salts of formula



X is branched C₃-C₂₀alkyl or C₃-C₈cycloalkyl;

X₁ is hydrogen, linear C₁-C₂₀alkyl, branched C₃-C₂₀alkyl or C₃-C₈cycloalkyl; with the proviso that the sum of the carbon atoms in X and X₁ is at least 4;

Y is linear C₁-C₁₀alkyl, branched C₃-C₁₀alkyl or C₃-C₈cycloalkyl;

A⁻ is a non-nucleophilic anion, selected from the group (BF₄)⁻, (SbF₆)⁻, (PF₆)⁻, (B(C₆F₅))₄⁻, C₁-C₂₀alkylsulfonate, C₂-C₂₀haloalkylsulfonate, unsubstituted C₆-C₁₀arylsulfonate, camphor-sulfonate, C₁-C₂₀-perfluoroalkylsulfonylmethide, C₁-C₂₀-perfluoroalkylsulfonylimide, and C₆-C₁₀arylsulfonate substituted by halogen, NO₂, C₁-C₁₂alkyl, C₁-C₁₂halo-alkyl, C₁-C₁₂alkoxy or by COOR₁; and

R₁ is C₁-C₂₀alkyl, phenyl, benzyl; or phenyl mono- or poly-substituted by C₁-C₁₂alkyl, C₁-C₁₂alkoxy or by halogen.

The commercially available bisaryl iodonium salts are Irgacure 250 (iodonium, (4-methyl-phenyl)[4-(2-methylpropyl)phenyl]-, hexafluorophosphate(1-) from Ciba Specialty Chemicals), CD 1012 (Sartomer), UV 9380C (GE Bayer Silicones), Rhodorsil 2074 (Rhodia) etc, and triaryl sulfonium salts are UVI-6990, UVI-6974 (Union Carbide) etc.

Emphasized are hybrid systems that contain cationically and radically polymerisable and photopolymerisable raw materials. Examples of cationically polymerisable systems include cyclic ethers, especially epoxides and oxetanes, and also vinyl ethers and hydroxy-

containing compounds. Lactone compounds and cyclic thioethers as well as vinyl thioethers can also be used. Further examples include aminoplastics or phenolic resole resins. These are especially melamine, urea, epoxy, phenolic, acrylic, polyester and alkyd resins, but especially mixtures of acrylic, polyester or alkyd resins with a melamine resin. Radiation curable resins contain ethylenically unsaturated compounds, especially (meth)acrylate resins.

Furthermore emphasized are hybrid systems that are photopolymerized in a first stage and then crosslinked through thermal post-treatment in a second stage. Such hybrid systems comprise an unsaturated compound in mixtures with non-photopolymerizable film-forming components. These may, for example, be physically drying polymers or solutions thereof in organic solvents, for example nitrocellulose or cellulose acetobutyrate. However, they may also be chemically or thermally curable resins, for example polyisocyanates, polyepoxides or melamine resins.

Furthermore emphasized are dual cure systems, which are cured first by heat and subsequently by UV or electron irradiation, or vice versa, and whose components contain ethylenic double bonds as described above capable to react on irradiation with UV light in presence of a photoinitiator.

Sometimes, it is also desirable to include, in addition to the primary photoinitiator, an additional photoinitiator and/or a co-initiators or synergists, for example photosensitisers that shift or broaden the spectral sensitivity. These include especially aromatic carbonyl compounds, for example benzophenone, thioxanthone, including especially isopropylthioxanthone, anthraquinone and 3-acylcoumarin derivatives, terphenyls, styryl ketones, and 3-(aroylmethylene)-thiazolines, camphorquinone and also eosin, rhodamine and erythrosine dyes.

Additional photoinitiators may be e.g. IRGACURE 184, 651, 369, 1700, 1800, and 1850 and DAROCUR 1173 and 4265 from Ciba-Specialty Chemicals INC.

The photoinitiator and occasionally the coinitiator are preferably present in an amount from 0.2 to 20 % by weight and most preferably between 1 and 10 %.

Ink jet inks of the present invention contain a colorant.

A wide variety of organic and inorganic dyes and pigments, alone or in combination may be selected for use in the ink jet ink compositions of this invention. The pigment particles should be sufficiently small (0.005 to 15 μ m) to permit free flow of the ink at the ejecting nozzles. The pigment particles should preferably be 0.005 to 1 μ m.

Very fine dispersions of pigments and their preparation are disclosed in e.g. US 5,538,548.

The pigment can be black, white, cyan, magenta, yellow, red, blue, green, brown, mixtures thereof, and the like. For example, suitable pigment materials include carbon blacks such as Regal 400R, Mogul L, Elftex 320 from Cabot Colo., or Carbon Black FW18, Special Black 250, Special Black 350, Special Black 550, Printex 25, Printex 35, Printex 55, Printex 150T from Degussa Co., and Pigment Black 7. Additional examples of suitable pigments are disclosed in, for example, U.S. 5,389,133.

Suitable white pigments are titanium dioxide (modifications rutil and anatas), e.g. KRONOS 2063 from Kronos, or HOMBITAN R610 L from Sachtleben.

Suitable pigments include, for instance, C. I. Pigment Yellow 17, C. I. Pigment Blue 27, C. I. Pigment Red 49:2, C. I. Pigment Red 81:1, C. I. Pigment Red 81:3, C. I. Pigment Red 81:x, C. I. Pigment Yellow 83, C. I. Pigment Red 57:1, C. I. Pigment Red 49:1, C. I. Pigment Violet 23, C. I. Pigment Green 7, C. I. Pigment Blue 61, C. I. Pigment Red 48:1, C. I. Pigment Red 52:1, C. I. Pigment Violet 1, C. I. Pigment White 6, C. I. Pigment Blue 15, C. I. Pigment Yellow 12, C. I. Pigment Blue 56, C. I. Pigment Orange 5, C. I. Pigment Black 7, C. I. Pigment Yellow 14, C. I. Pigment Red 48:2, C. I. Pigment Blue 15:3, C. I. Pigment Yellow 1, C. I. Pigment Yellow 3, C. I. Pigment Yellow 13, C. I. Pigment Orange 16, C. I. Pigment Yellow 55, C. I. Pigment Red 41, C. I. Pigment Orange 34, C. I. Pigment Blue 62, C. I. Pigment Red 22, C. I. Pigment Red 170, C. I. Pigment Red 88, C. I. Pigment Yellow 151, C. I. Pigment Red 184, C. I. Pigment Blue 1:2, C. I. Pigment Red 3, C. I. Pigment Blue 15:1, C. I. Pigment Blue 15:3, C. I. Pigment Blue 15:4, C. I. Pigment Red 23, C. I. Pigment Red 112, C. I. Pigment Yellow 126, C. I. Pigment Red 169, C. I. Pigment Orange 13, C. I. Pigment Red 1-10, 12, C. I. Pigment Blue 1:X, C. I. Pigment Yellow 42, C. I. Pigment Red 101, C. I. Pigment

Brown 6, C. I. Pigment Brown 7, C. I. Pigment Brown 7:X, C. I. Pigment Black 11, C. I. Pigment Metal 1, C. I. Pigment Metal 2, C.I. Pigment Yellow 128, C.I. Pigment Yellow 93, C.I. Pigment Yellow 74, C.I. Pigment Yellow 138, C.I. Pigment Yellow 139, C.I. Pigment Yellow 154, C. I. Pigment Yellow 185, C.I. Pigment Yellow 180, C.I. Pigment Red 122, C.I. Pigment Red 184, and bridged aluminum phthalocyanine pigments, C. I. Pigment Red 254, C. I. Pigment Red 255, C.I. Pigment Red 264, C. I. Pigment Red 270, C.I. Pigment Red 272, C. I. Pigment Violet 19, C.I. Pigment Red 166, C.I. Pigment Red 144C, C. I. Pigment Red 202, C. I. Pigment Yellow 110, C. I. Pigment Yellow 128, C. I. Pigment Yellow 150, C.I. Pigment Orange 71, C. I. Pigment Orange 64, C. I. Pigment Blue 60.

The pigment may, but need not, be in the form of a dispersion comprising a dispersant also called pigment stabilizer. The latter may be, for example, of the polyester, polyurethane or polyacrylate type, especially in the form of high molecular weight block copolymer, and would typically be incorporated at 2.5% to 100% by weight of the pigment. An example of a polyurethane dispersant is EFKA 4047.

Further pigment dispersions are (UNISPERSE, IRGASPERSE) and ORASOL Dyes (solvent soluble dyes): C.I. Solvent Yellow 146, C.I. Solvent Yellow 88, C.I. Solvent Yellow 89, C.I. Solvent Yellow 25, C.I. Solvent Orange 11, C.I. Solvent Orange 99, C.I. Solvent Brown 42, C.I. Solvent Brown 43, C.I. Solvent Brown 44, C.I. Solvent Red 130, C.I. Solvent Red 233, C.I. Solvent Red 125, C.I. Solvent Red 122, C.I. Solvent Red 127, C.I. Solvent Blue 136, C.I. Solvent Blue 67, C.I. Solvent Blue 70, C.I. Solvent Black 28, C.I. Solvent Black 29

Especially emphasized are the MICROLITH-pigment preparations commercially available from Ciba Specialty Chemicals Inc. These pigment dispersions may be organic or inorganic pigments predispersed in a variety of resins, e.g. in vinyl resins, acrylic resins and aromatic polyurethane resins. MICROLITH-WA may for example be a line of pigments predispersed in alkaline water/alcohol soluble acrylic resin (specially developed for aqueous gravure and flexographic printing) with pigments that may be compatible with UV and ink jet printing inks.

The Microlith-K ink jet products are used in vinyl-based inks, which can be formulated to give good adhesion to many substrates, from plasticized and rigid PVC, metal foils, to polymer coated regenerated cellulose films.

Ink Jet inks of the present invention may also more generally include others pigments preparation like chips or in situ combination during grinding of pigments (as described above) and hyperdispersants (e.g. Solsperse as available from Avecia) into the binder carrier.

Other Additives

Ink jet inks of the present invention may include additives such as surfactants, biocides, buffering agents, anti-mold agents, pH adjustment agents, electric conductivity adjustment agents, chelating agents, anti-rusting agents, polymerisation inhibitors, light stabilizers, and the like. Such additives may be included in the ink jet inks of the present invention in any effective amount, as desired.

Compositions according to the present invention may contain organic solvents, for example, ketones, ethers and esters, such as methyl ethyl ketone, isobutyl methyl ketone, cyclopentanone, cyclohexanone, N-methylpyrrolidone, dioxane, tetrahydrofuran, 2-methoxyethanol, 2-ethoxyethanol, 1-methoxy-2-propanol, 1,2-dimethoxyethane, ethyl acetate, n-butyl acetate and ethyl 3-ethoxypropionate or 1-Isopropyl-2,2-dimethyltrimethylendiisobutyrate available as TXIB from Eastman.

Apparatuses for radiation curing are known to those skilled in the art and are commercially available. For example, the curing proceeds with high-, medium- and low-pressure mercury radiators, mercury vapour lamps or pulsed xenon lamps. An intensity of 40 to 240 W/cm in the 200-400 nm region is usually employed.

Further examples are: microwave-excited metal vapour lamps, excimer lamps, superactinic fluorescent tubes, fluorescent lamps, argon incandescent lamps, flash lamps, e.g. high-energy flash lamps, photographic floodlight lamps, light-emitting diodes (LED), electron beams and X-rays, laser light sources, for example excimer lasers.

The distance between the lamp and the substrate to be exposed may vary according to the intended use and the type and strength of the lamp and may be, for example, from 2 cm to 150 cm.

The ink jet receiver materials to which the ink composition of the present invention can be jetted are not limited and include e.g. paper, coated paper, polyolefin coated paper, cardboard, wood, composite boards, plastic, coated plastic, canvas, textile, metal, glass, and ceramics.

Example 1: according to PCT Application No. EP/02/12160

Preparation of a crystalline isomeric mixture (formulae Ia and IIa) containing water of crystallisation

1.1) Friedel-Crafts reaction

109.4 g (0.65 mol) of diphenylmethane, 159.3 g (1.495 mol) of isobutyric acid chloride and 150 ml of 1,2-dichlorobenzene are combined and cooled to 5-0°C. In the course of about four hours, 208.0 g (1.56 mol) of aluminium chloride are added in small portions at an internal temperature of 5-0°C. HCl gas is evolved. Stirring is then carried out for about 16 hours at an internal temperature of 0-5°C. At the end of that period, all the aluminium chloride has dissolved. The dark-red reaction mixture is then poured onto ice and water and stirred to complete the reaction. The two phases are separated in a separating funnel. The organic phase is washed with water and then concentrated for a short time in a vacuum rotary evaporator at about 60°C and about 25 mbar. 403.1 g of a yellow liquid are obtained. The product, an isomeric mixture with bis[4-(2-methyl-propionyl)-phenyl]-methane as the main component, is used in the next reaction without being purified further. Excluding the solvent 1,2-dichlorobenzene, 87.3 % p,p-isomer, 11.4 % m,p-isomer, 0.66 % m,m-isomer and 0.60 % p-mono compound are found in the GC and ¹H-NMR spectrum.

1.2) Enol chlorination

403.1 g (0.65 mol) solution of the isomeric mixture of bis[4-(2-methyl-propionyl)-phenyl]-methane with [3-(2-methyl-propionyl)-phenyl]-[4-(2-methyl-propionyl)-phenyl]-methane from the Friedel-Crafts reaction are heated to 55-60°C by means of an oil bath. 92.2 g (1.30 mol) of chlorine gas are then introduced through a glass frit at 55-60°C, with thorough stirring, more rapidly at the beginning and only slowly at the end. HCl gas is evolved. The duration of the introduction is about 6 hours. 441.5 g of a yellowish liquid are obtained. The product, an isomeric mixture with bis[4-(2-chloro-2-methyl-propionyl)-phenyl]-methane as the main component, is used in the next reaction without being purified further. Excluding the solvent 1,2-dichlorobenzene, about 87 % p,p-isomer and about 12 % m,p-isomer are found in the ¹H-NMR spectrum.

1.3) Hydrolysis

Rapid crystallisation for working-up of the hydrolysis product

208.0 g (1.56 mol) of NaOH concentrated to 30 % and 208 ml of deionised water and 205.7 g of methanol are combined. There are then added dropwise at 50°C in a period of about one hour, with thorough stirring, 441.5 g (0.65 mol) of a solution, in 1,2-dichlorobenzene, of the isomeric mixture of bis[4-(2-chloro-2-methyl-propionyl)-phenyl]-methane with [3-(2-chloro-2-methyl-propionyl)-phenyl]-[4-(2-chloro-2-methyl-propionyl)-phenyl]-methane from the chlorination reaction, additionally diluted with 102.8 g of methanol. The internal temperature slowly rises to 55-60°C. The alkaline mixture (about pH 12) is then stirred for about three to four hours at 55-60°C. The conversion is checked with a GC sample and a ¹H-NMR sample. The mixture is then cooled to 45°C and adjusted dropwise to a pH of about 2-3 with about 63.5 g of 16 % hydrochloric acid. The colour of the emulsion changes from a strong yellow to yellow. The mixture is then stirred for about 30 minutes. When the hydrolysis is complete, the reaction mixture is neutralised with a small amount of dilute sodium hydroxide solution. The two phases are separated at about 50°C in a separating funnel. 200 ml of water are added to the organic phase, which is then stirred and separated off again. The organic phase is the solution of an isomeric mixture with bis[4-(2-hydroxy-2-methyl-propionyl)-phenyl]-methane as the main component. About 88 % p,p-isomer and about 11 % m,p-isomer are found in the ¹H-NMR spectrum. The warm organic phase is diluted with solvent (400 ml of toluene), and a small amount of water (about 23 g of water, about 10 % of the amount of end product) is added thereto. The solution is seeded at 40-35°C with water-containing crystals and is later cooled after the crystallisation. The thick suspension is filtered and washed with toluene and hexane in order to displace the 1,2-dichlorobenzene. The crystals are dried *in vacuo* to constant weight. 177.7 g of white crystals containing water of crystallisation are obtained. This corresponds to a yield of 76.3 % of theory (358.44) over all three reaction steps. The crystals of the isomeric mixture melt at 68-70°C and contain 5.02 % by weight water. The crystals exhibit an X-ray powder spectrum with the characteristic lines at a 2-theta angle of 6.69; 9.67; 13.95; 15.11; 16.35; 17.57; 19.43; 21.39; 22.17; 23.35; 25.93; 27.11; 27.79; 28.73; 34.83; 41.15.

Change of solvent after hydrolysis and adjustment of the ratio of isomers in the crystals
Analogously to Example 1, diphenylmethane is acylated with isobutyric acid chloride in 1,2-dichlorobenzene, then the diketone mixture is chlorinated without intermediate purification, and hydrolysis is finally carried out with sodium hydroxide solution and with the addition of methanol. The distribution of isomers in the reaction mixture between the para-para compound and the meta-para compound, about 12 % meta-para compound, is maintained

over all three steps, because no product is separated off until crystallisation. After separation of the aqueous phase, the organic phase, in a modification of Example 1, is subjected to steam distillation at about 95-100°C, and the 1,2-dichlorobenzene is removed. About 154 g of 1,2-dichlorobenzene are recovered. There is obtained a thick yellow oil, which tends to crystallise with water below 60°C. The oil is crystallised with a large amount of water without further solvent. Slow cooling yields moist, light-yellow spherules, which are filtered off and dried *in vacuo* at about 35-40°C. In the ¹H-NMR spectrum of the crystals, the distribution of isomers between the para-para compound and the meta-para compound is the same as in the ¹H-NMR spectrum of a sample of the oil, i.e. about 88 % para-para isomer and about 12 % meta-para isomer. It no longer contains any 1,2-dichlorobenzene to interfere with the evaluation of the ¹H-NMR spectrum. The light-yellow crude product is also surprisingly pure in the TLC. There are obtained 222.9 g of yellowish granules, which melt at 63-72°C. This corresponds to a yield of 95.7 % over three reaction steps with a starting batch size of 0.65 mol (Example 1f).

From that crude product, by means of controlled crystallisations from water with variously small additions of toluene, it is possible to produce products having selected compositions of the isomers. Accordingly, a portion of the meta-para compound can be filtered off with the variously small amounts of toluene. From the toluenic filtrate and its isomeric composition in the ¹H-NMR spectrum, as well as the amount of crystals and their isomeric composition in the ¹H-NMR spectrum, it is possible to calculate and confirm the isomeric composition in the crystals more exactly.

Application example

UV inkjet test formulation

A pigment concentrate was prepared in a bead mill using the raw materials shown in Table 1. 15 parts of the pigment concentrate were mixed with 79.50 parts of the reactive diluent (Viajet 400, UCB), 0.40 parts levelling agent (DOW Corning 57, DOW Corning), and 6 or 8 parts of the photoinitiator, to give the final ink.

Table 1. Composition of the pigment concentrate.

Raw Material	Parts
Viajet 100 (UCB)	78.45
Irgalite Blue GLO (Ciba)	20.00
Florstab UV1 (Kromachem)	1.00
Solsperse 5000 (Avecia)	0.55

ViaJet 100 is a unique, 100% solids pigment grinding vehicle for use in producing pigment concentrates for UV inkjet inks.

Florstab is an in-can stabilizer for UV-curing systems

Curing performance of the UV Inkjet test formulations

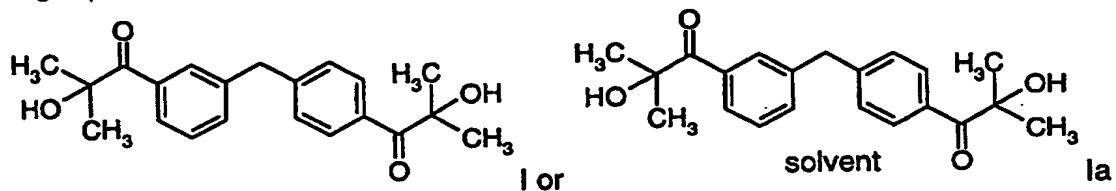
The inks were applied to metallized paper using a 12 μ m K-bar. Upon exposure to the UV light of 2 medium pressure mercury lamps (120 W/cm each), the surface cure of the inks has been tested (dry rub test with paper tissue). The cure speed corresponds to the maximum speed of the conveyor belt of the UV curing unit, at which the ink was completely cured and tack free. The observed data are shown in Table 2.

Table 2. Cure speed of the UV Inkjet test formulations.

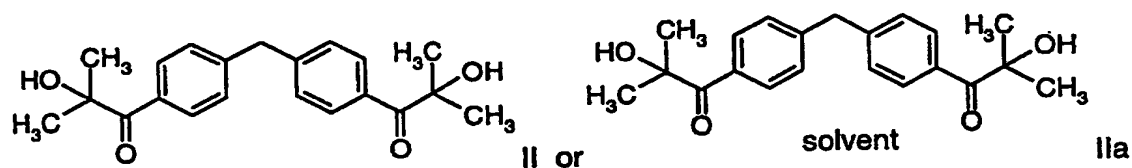
Photoinitiator	Cure Speed [m/min]	
	6%	8%
Irgacure 369	20	30
Irgacure 907/ITX (4:1)	20	30
Photoinitiator of Example 1	30	60

Claims

1. An ultraviolet curable ink jet ink composition comprising a photopolymerizable monomer, oligomer or prepolymer; a colorant and a compound of the formula I or II or Ia or IIa



or



or mixtures thereof.

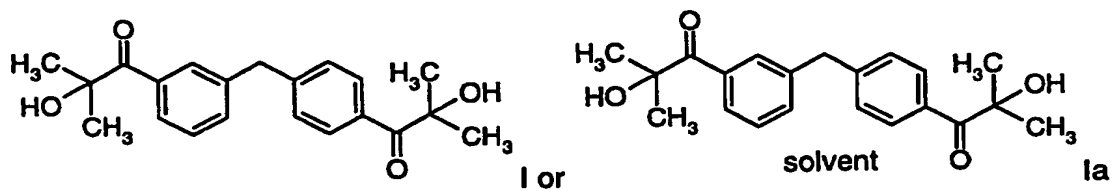
2. An ink-jet ink composition according to claim 1, comprising a mixture of compound Ia and IIa having a content of compound Ia of 1-2% by weight and a water content of 4-6% by weight.

3. The use of a composition according to claim 1 in ink jet ink systems.

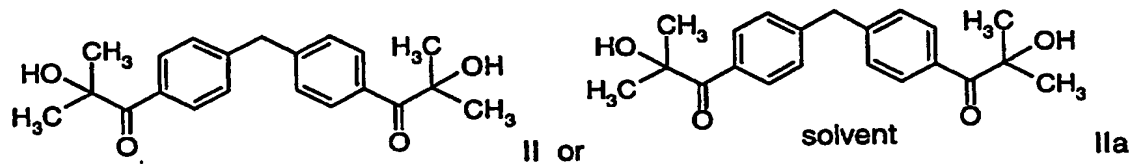
II/2-22872/P1

Abstract

The invention relates to an ultraviolet curable ink jet ink composition comprising a photopolymerizable monomer, oligomer or prepolymer; a colorant and a compound of the formula I or II or Ia or IIa



or



or mixtures thereof.

PCT/EP2004/050450

